SEC-MALS characterization of natural rubber: study of phenomena behind the abnormal elution profile

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Natural and synthetic poly(cis-1,4-isoprene) were characterized by size exclusion chromatography coupled with an online multiangle light scattering detector (SEC-MALS) (Fig. 1). Different from SEC classic method, the absolute molar masses are directly determined according to the variation of scattered light intensities with detecting angles and by using Zimm plot method for zero-angle extrapolation. This technique allows us to obtain elution profiles of rubber samples.

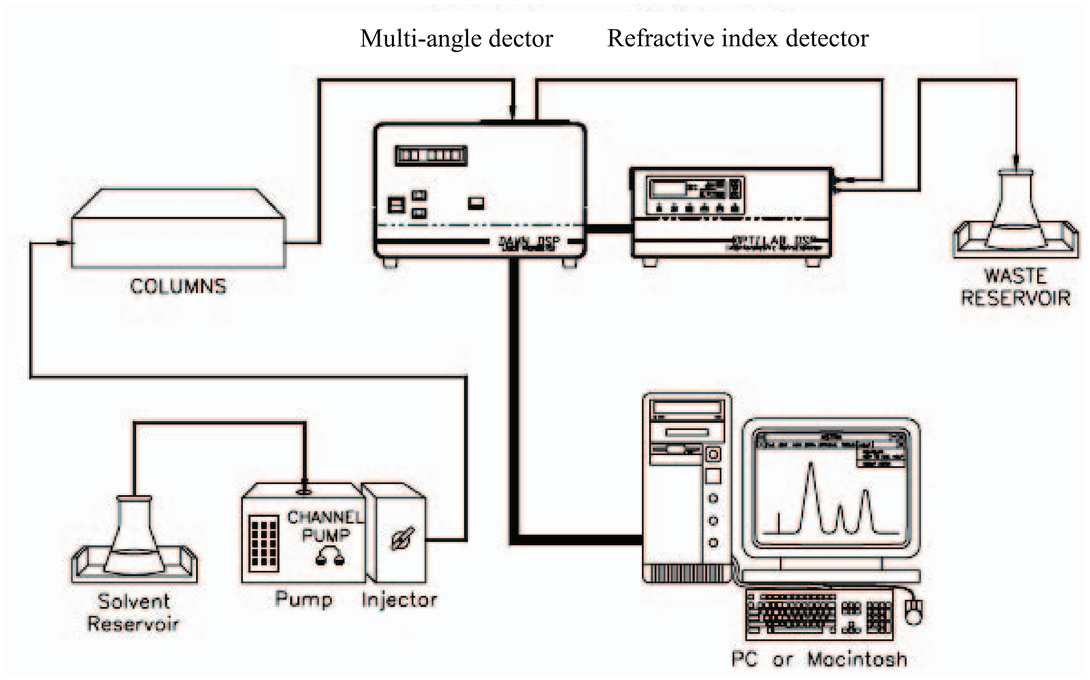

Fig. 1: The DAWN online with a SEC system [1].

Results and discussion

Contrary to synthetic poly(*cis*-1,4-isoprene) (SR), natural rubber (NR) samples showed anomalous elution profiles (Fig. 2). The beginning of the elution was very close to SR but, after a certain elution volume, the molar masses of the eluting macromolecules increased with elution volume instead of continuing to decrease, which resulted in a upturn curve profile. Adding tetrabutylamonium bromide (TBA) in THF (solvent and mobile phase) removed this phenomenon (Fig. 3). In addition, using different concentrations of TBA showed that TBA had two simultaneous actions: reducing the abnormal elution profiles and the quantity of aggregates (insoluble part or gel) (Fig. 4).

Conclusion

These results show that the main phenomena involved in the abnormal elution was delayed entities adsorbing on the column packing. Their delaying elution was responsible for the artificially increased of molar masses especially at high elution volumes. Therefore, the SEC classic method calibrated with synthetic polyisoprene could cause error of calculation of molar masses of natural rubber.

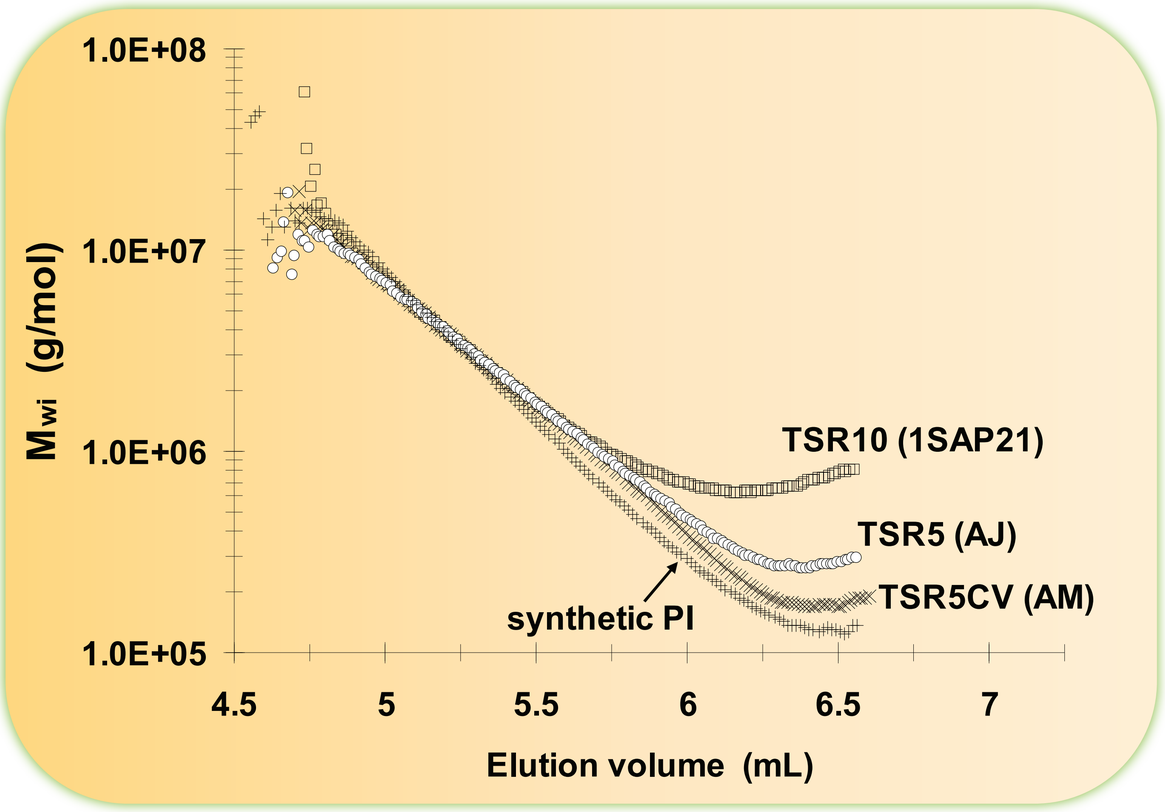

Fig. 2: Plots of weight-average molar masses (M_{wi}) against elution volume for the three NR samples and a synthetic poly(*cis*-1,4-isoprene) (Natsyn 2200).

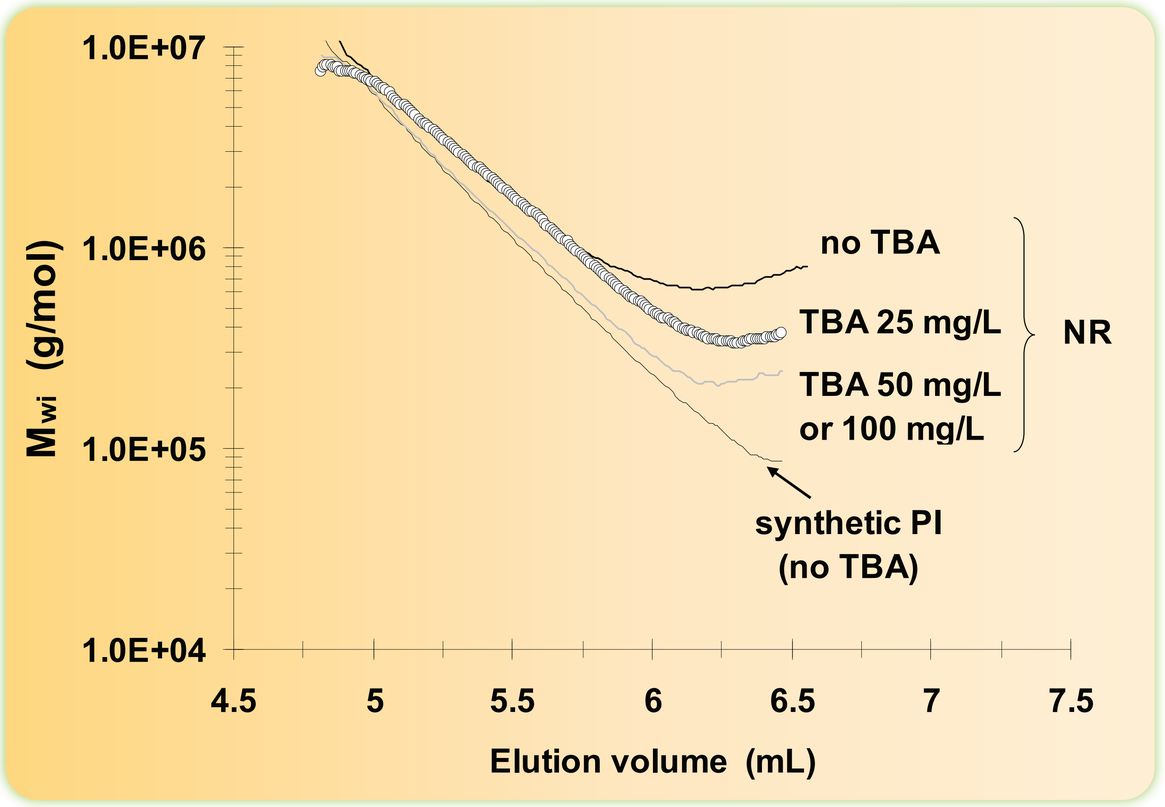

Fig. 3: Plots of the molar masses (Mwi) against elution volume for a synthetic poly(*cis*-1,4-isoprene) (Natsyn 2200) and a NR sample (1SAP21) analyzed with different concentrations of TBA in THF.

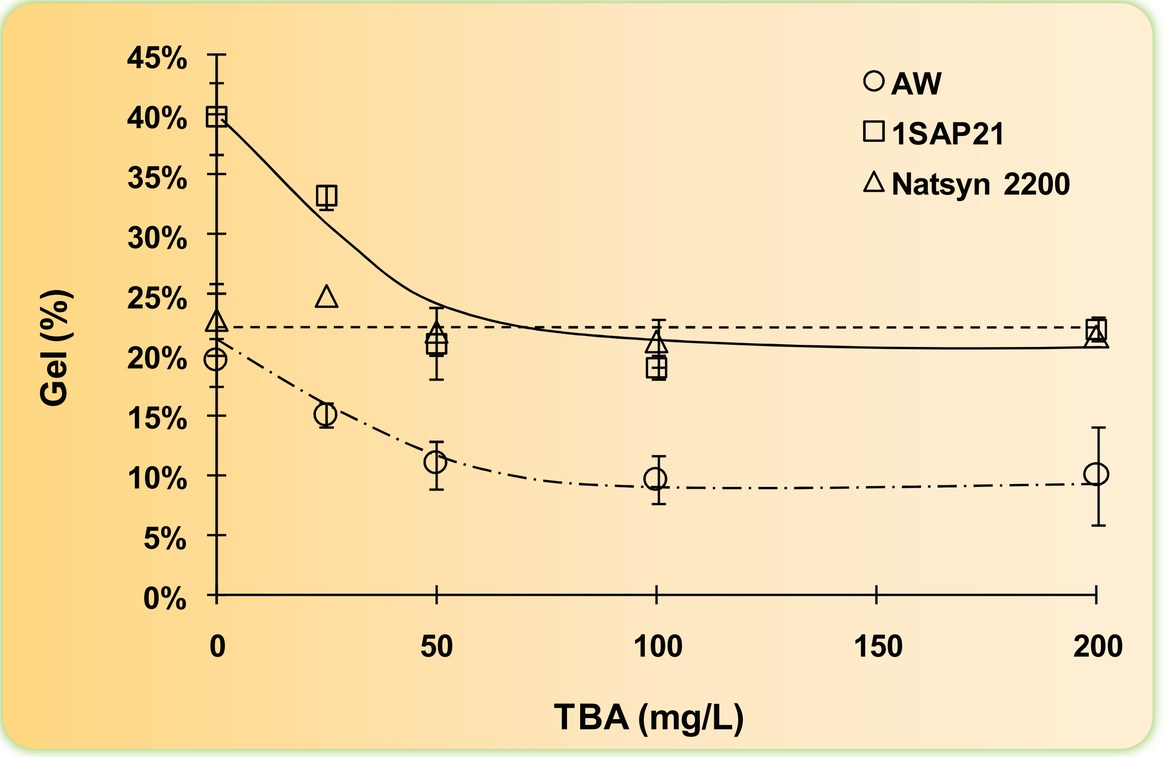

Fig. 4: Effect of TBA concentration in THF on the gel rate for the two NR samples (AM, 1SAP21) and a synthetic poly(*cis*-1,4-isoprene) sample (Natsyn 2200).

Reference

[1] Hardware Manual for the Dawn DSP Light Scattering Instrument - Wyatt Technology M2000 Rev. A.